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STATISTICAL FLUCTUATION OF INTENSITY IN DEBYE-SCHERRER
LINES DUE TO RANDOM ORIENTATION OF CRYSTAL GRAINS

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SUMMARY

In the Debye-Scherrer diagram of a stationary polycrystalline sample, the intensity distribution in the line is erratic because of statistical irregularities of the crystal grain orientation. The fluctuations of intensity are discussed for the case that the only causes of line breadth are the natural spectral width of the primary radiation and the finite size of the grains (i.e., pure Fraunhofer diffraction). The mean deviation of the centroid of the intensity curve from the Bragg angle for the strongest wave length can be considered as the error in measuring the line. This deviation is theoretically estimated. For a typical case, namely, grains of 2×10^{-4} centimeter length and 1-square-millimeter irradiated area, the error is found to be about 10 times smaller than that reported in experimental literature.

INTRODUCTION

A stationary polycrystalline aggregate of crystals gives rise to an intensity distribution in the Debye-Scherrer line which depends on the number of grains being in reflecting position. In general, a line of erratic shape is obtained with no well-defined maximum. This difficulty is usually avoided either by rotating or oscillating the sample about an axis normal to the incident beam (thus averaging out the statistical irregularities) or by choosing the effective number of grains so large that the relative fluctuations become negligible.

In some cases, however, neither of these devices is practicable. In particular, for stress measurements, sample rotation (or, what amounts to the same, oscillation of the tube) is often cumbersome, and the grain size of the sample is not subject to choice. But in other cases too, for instance, with focusing arrangements, the irregularities of crystal orientation cause difficulties, particularly when high resolution is obtained by the use of high diffraction angles or large distances between sample and film.

In the following, the error in the measurement of the line center, due to these irregularities, is estimated. For this purpose, a definite geometric condition must be chosen which determines the intensity diffracted by a single crystal grain in a general orientation. In most cases, the width and divergence of the incident beam will be the main determining factors for this intensity. However, for very high resolution, these geometric factors become small in comparison with the width due to the spectral impurity of the primary radiation (reference 1) and it is in this case precisely that the question of accuracy becomes most important. Consequently, a primary beam of negligible width and divergence is assumed so that the recorded intensity depends only on the angle of diffraction; that is, pure Fraunhofer diffraction is considered. The crystal grains are assumed small enough so that the kinematic theory can be used. The crystal shape is assumed spherical with a uniform diameter.

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DIFFRACTION BY A SINGLE CRYSTAL GRAIN

In figure 1, O is the origin of the reciprocal lattice, and B is the position of the reciprocal lattice point belonging to a Bragg lattice distance d . For a given crystal lattice, B can have any position on a sphere of radius $1/d$ and center O . The Laue spheres belonging to different wave numbers k_1 , k_0 , and k_2 have the centers F_1 , F_0 , and F_2 , respectively. If k_0 is the mean wave number of the primary radiation (corresponding to the maximum spectral intensity), then the strongest reflection will take place when B is situated on the intersection of the Laue sphere with center F_0 and the "reflection sphere" with center O and radius $1/d$. The diffraction maximum will occur at the angle ϑ_0 so that $\angle POC = \frac{\pi}{2} - \vartheta_0$. The intensity will decrease rapidly as ϑ deviates from this value. Similarly, positions of B which are far from the intersection (point C of fig. 1) will contribute little intensity. Therefore, all angular distances from the point C can be considered small.

Returning to a general wave number k , consider the intensity of wave number k diffracted in a direction given by the point A and caused by a crystal position indicated by the point B . Let B have the polar coordinates $1/d$, $\pi/2 - \vartheta + \gamma$, and O with respect to the origin O , and let the point A have the polar coordinates $2k \sin \vartheta$, $\pi/2 - \vartheta$, and ψ . With the assumption of spherical shape, the intensity will be a function of the distance $R = AB$.

The following equation is obtained

$$R^2 = \frac{1}{d^2} + 4k^2 \sin^2 \vartheta - \frac{4k}{d} \sin \vartheta \cos \gamma + (1 - \cos \psi) \sin 2\vartheta \cos (\vartheta - \gamma) \quad (1)$$

If Ψ^2 is the interference function, the intensity of wave number k diffracted in the direction ϑ is

$$J_k \propto \Psi^2(R) \quad (2)$$

Let the spectral intensity distribution be given by the function $f(k)$. Then the total intensity of all wave lengths is proportional to

$$\int f(k) \Psi^2(R) dk \quad (3)$$

where R is considered as a function of k according to equation (1). In most measurements of this type, the film is rotated about the primary beam so that intensities belonging to a definite ϑ are averaged with respect to the azimuthal angle. This fact may be taken into account by integrating the expression (3) over all azimuthal angles ψ of the reciprocal lattice point. The intensity becomes:

$$J \propto \int_0^{2\pi} \int_0^\infty d\psi dk f(k) \Psi^2(R) \quad (4)$$

The exact form of the interference function Ψ was calculated by Patterson (reference 2). It shall, as usual, be replaced for mathematical convenience by a Gaussian function $Ce^{-\alpha R^2}$ of identical ratio of maximum to the integral of the squared function. This requires (reference 2) that

$$\alpha = \rho^2 \pi \left(\frac{4\pi}{3} \right)^{2/3} = 8.16\rho^2 \quad (5)$$

where ρ is the radius of the crystal grain. For mathematical convenience, the resonance curve $f(k)$ which represents the spectral shape

of the characteristic radiation will also be replaced by a Gaussian curve so that the two curves have the same half-value width. If w is the measured half-value width in the scale of the wave lengths λ , the function $f(k)$ will be

$$f(k) = \frac{1}{(k - k_0)^2 + (k_0^2 w/2)^2} \quad (6)$$

and this function has the same half-value width as $e^{-\beta(k-k_0)^2}$ if

$$\beta = \frac{4 \log_e 2}{w^2 k_0^4} = \frac{2.76}{w^2 k_0^4} \quad (7)$$

Equation (4) now takes the form:

$$\begin{aligned} J &\propto \int_0^{2\pi} \int_0^\infty d\psi \, dke^{-\alpha R^2} e^{-\beta(k-k_0)^2} \\ &= \int_0^\infty dke^{-\beta(k-k_0)^2} e^{-\alpha R_0^2} \int_0^{2\pi} e^{-\alpha(1-\cos\psi)\sin 2\vartheta \cos(\vartheta-\gamma)} d\psi \\ &= \int_0^\infty I_0(\alpha g k) e^{-\alpha g k} e^{-\beta(k-k_0)^2} e^{-\alpha k_0^2} dk \end{aligned} \quad (8)$$

where

$$g = \frac{2}{d} \cos(\vartheta - \gamma) \sin 2\vartheta \quad (9)$$

$$R_0^2 = \frac{1}{d^2} + 4k^2 \sin^2 \vartheta - \frac{4k}{d} \sin \vartheta \cos \gamma \quad (10)$$

Since only the close surrounding of $k = k_0$ will contribute substantially to the integral (8), the limit of integration may be changed to $\int_{-\infty}^{+\infty}$. Furthermore, if $\sin 2\vartheta$ is not too small, the function $I_0(\alpha g k) e^{-\alpha g k}$ is slowly variable and can be replaced by the constant $I_0(\alpha g k_1) e^{-\alpha g k_1}$ where

$$k_1 = \frac{\beta k_0 + \frac{2\alpha}{d} \sin \vartheta \cos \gamma}{\beta + \alpha \sin^2 \vartheta} \quad (11)$$

is the value of k where the exponential factor in the integrand attains its maximum value.

There can be written

$$J \propto I_0(\alpha g k_1) e^{-\alpha g k_1} \int_{-\infty}^{+\infty} e^{-\beta(k-k_0)^2 - \alpha k_0^2} dk \quad (12)$$

or by equation (10):

$$J \propto I_0(\alpha g k_1) e^{-\alpha g k_1} \sqrt{\frac{\pi}{\beta + 4\alpha \sin^2 \vartheta}} e^{-D} \quad (13)$$

where

$$D = \beta k_0^2 + \frac{\alpha}{d^2} - \frac{\left(2\beta k_0 + \frac{4\alpha}{d} \sin \vartheta \cos \gamma\right)^2}{4(\beta + 4\alpha \sin^2 \vartheta)} \quad (14)$$

Putting

$$\sin \vartheta = \frac{1}{2k_0 d} \quad (15)$$

$$\sin \vartheta = \sin \vartheta_0 + \Delta \sin \vartheta \quad (16)$$

and

$$\cos \gamma = 1 - \frac{\gamma^2}{2} \quad (17)$$

expression (14) is expanded up to second-order quantities $(\Delta \sin \vartheta)^2$ and γ^2 to obtain:

$$D = 4\alpha k_0^2 \left(\gamma^2 \sin^2 \vartheta_0 + \frac{\beta (\Delta \sin \vartheta)^2}{4\alpha \sin^2 \vartheta_0 + \beta} \right) \quad (18)$$

SHAPE OF DIFFRACTION LINE

The spatial orientation of a crystal grain is characterized by the position of a crystallographic direction on the unit sphere. If the direction (hkl) corresponding to the reciprocal lattice point B is chosen as characteristic for the orientation of a crystal grain, then the set of representative points on the unit sphere will determine the diffracted intensity. The unit sphere is subdivided into small cells of area Δ^2 (fig. 2).

The intensity diffracted by directions (hkl) which form angles from φ to $\varphi + \Delta$ with the primary beam will be proportional to the number of representative points situated on a circular ring of width Δ (fig. 2). If this number is n_φ , the total intensity diffracted in a direction ϑ by planes (hkl) is

$$\sum n_\varphi J(\varphi, \vartheta)$$

where J is the intensity given by equation (13). According to figures 1 and 2, the connection between γ and φ is

$$\varphi = \gamma + \frac{\pi}{2} - \vartheta \quad (19)$$

Since there are always crystallographic directions which, for diffraction, are equivalent to a given direction (hkl) ,¹ all contributions to the intensity have not yet been counted. The contributions of all those crystals whose equivalent directions form an angle ϕ with the primary beam should be added. Since only random orientations have to be dealt with, this is done easily by multiplying the number n_ϕ' by s , the number of equivalent planes. If

$$n_\phi = n_\phi' \cdot s \quad (20)$$

the total intensity becomes

$$J_t = \sum_{\phi} n_\phi J(\phi, \vartheta) \quad (21)$$

The exact shape of the intensity curve is unimportant, but determining that angle ϑ which experimentally appears to be the center of the line is necessary. This requires the definition of the experimental procedure by which the center of an irregular diffraction line is measured. In fact, most measurements of this type are visual. For the present purpose, a more quantitative method, at least in principle, is obviously needed. Actually, it may well turn out that the more refined methods of objective measurements are unnecessary because the inherent error is large. However, the aim at present is to calculate the best possible accuracy with a given crystal aggregate.

Probably the best experimental procedure would be to find, by the method of least squares, that resonance or Gaussian curve which fits best a measured intensity curve, but this method is so cumbersome that the line center has been defined herein as its center of gravity or centroid ξ which is given by

$$\xi \int J_t d\vartheta = \int \vartheta J_t d\vartheta \quad (22)$$

The integration should be extended over "the line" - an ill-defined quantity since the intensity between two lines is the sum of the intensities belonging to the two, or even more, nearest lines. This difficulty is typical for the precise characterization of a line. The definition (22) is meaningful only if the intensity between two lines decreases to

¹According to Friedel's law, there is at least one equivalent direction $(-h, -k, -l)$.

a negligible value, in which case the integral must be extended into this region of substantially zero intensity, and the exact position of the limiting point does not matter. It must be assumed that such a region exists.

CRYSTAL STATISTICS

The N crystal grains of identical shape are oriented at random. The probability that there are n_ϕ grains whose directions (hkl) form an angle ϕ to $\phi + \Delta$ with the primary beam is that of n_ϕ balls out of N falling into a box of area $2\pi \Delta \cdot \sin \phi$ when they are thrown at random into a total area 4π . It is

$$P_{n_\phi} = \left(\frac{\Delta}{2} \sin \phi\right)^{n_\phi} \left(1 - \frac{\Delta}{2} \sin \phi\right)^{N-n_\phi} \frac{N!}{n_\phi!(N-n_\phi)!} \quad (23)$$

As explained above, the existence of s equivalent lattice planes modifies the situation by substituting the effective number sN of grains for N . The mean number \bar{n}_ϕ is

$$\bar{n}_\phi = \frac{s\Delta \cdot N \sin \phi}{2} \quad (24)$$

and, from equation (23), one concludes in the usual way,

$$\overline{(\Delta n_\phi)^2} = \overline{(n_\phi - \bar{n}_\phi)^2} = \bar{n}_\phi = \frac{s\Delta \cdot N \sin \phi}{2} \quad (25)$$

The mean square deviation of the position of the centroid from its mean value is now considered. If ϑ_0 is taken as origin of the angular coordinate, the mean value of ξ is zero, and

$$\xi \int J_t d(\Delta \vartheta) = \int \Delta \vartheta \cdot J_t(\vartheta) d(\Delta \vartheta) \quad (26)$$

The coefficient of ξ is the "integrated intensity" of the line. It is also subject to statistical fluctuations but clearly these fluctuations are of minor importance for the value of $\overline{\xi^2}$, and $\int J_t d(\Delta\vartheta)$ may be replaced by its mean value. The following expression is obtained for $\overline{\xi^2}$ by equation (21):

$$\overline{\int J_t d(\Delta\vartheta)^2 \xi^2} = \overline{\left[\int (\Delta\vartheta) J_t(\vartheta) d(\Delta\vartheta) \right]^2} = \overline{\left[\sum_i n_i \int J(\varphi_i, \vartheta) (\Delta\vartheta) d(\Delta\vartheta) \right]^2} \quad (27)$$

where the index i corresponding to the angle φ_i has been substituted for the general index φ .

If

$$\int J(\varphi_i, \vartheta) (\Delta\vartheta) d(\Delta\vartheta) = f(\varphi_i) \quad (28)$$

and

$$\overline{\left[\int J_t d(\Delta\vartheta) \right]^2} = c \quad (29)$$

then

$$c \overline{\xi^2} = \overline{\sum_{i,k} n_i n_k f(\varphi_i) f(\varphi_k)} = \sum_{i,k} \overline{n_i n_k} f(\varphi_i) f(\varphi_k) \quad (30)$$

In the double sum (30), the terms with $i = k$ and those with $i \neq k$ are separated so that

$$c \overline{\xi^2} = \sum_{i \neq k} \overline{n_i n_k} f(\varphi_i) f(\varphi_k) + \sum_i \overline{n_i^2} f^2(\varphi_i)$$

and, since by hypothesis the numbers n_i and n_k for $i \neq k$ are entirely independent,

$$\overline{C\xi^2} = \sum_{i \neq k} \overline{n_i} \overline{n_k} f(\varphi_i) f(\varphi_k) + \sum_i \overline{n_i^2} f^2(\varphi_i) \quad (31)$$

It is remembered that

$$\overline{n_i^2} = (\overline{n_i})^2 + (\overline{\Delta n_i})^2$$

so that, by equations (24) and (25),

$$\begin{aligned} \overline{C\xi^2} = \sum_{i \neq k} \left(\frac{s}{2}\right)^2 \cdot \sin \varphi_i \sin \varphi_k (\Delta \cdot N)^2 f(\varphi_i) f(\varphi_k) + \\ \sum_i f^2(\varphi_i) \left(1 + \frac{s\Delta \cdot N \sin \varphi_i}{2}\right) \frac{s\Delta \cdot N \sin \varphi_i}{2} \end{aligned} \quad (32)$$

It is now possible to pass to the limit $\Delta \rightarrow 0$:

$$\overline{C\xi^2} = \left(\frac{Ns}{2}\right)^2 \left(\int \sin \varphi f(\varphi) d\varphi\right)^2 + \frac{Ns}{2} \int \sin \varphi f^2(\varphi) d\varphi \quad (33)$$

since that part of the second sum in equation (32) which carries the factor Δ^2 vanishes in the limit.

Further simplifications are necessary in order to derive a simple result from equation (33). In equation (13), the factor preceding the Gaussian term e^{-D} will be considered constant since it is slowly variable in comparison with e^{-D} . Equation (13) becomes:

$$J \propto Ke^{-4\alpha k_0^2 \left[\gamma^2 \sin^2 \vartheta_0 + \frac{\beta (\Delta \sin \vartheta)^2}{4\alpha \sin^2 \vartheta_0 + \beta} \right]} \quad (34)$$

If

$$\Delta\varphi = \varphi - \varphi_0 = \varphi - \left(\frac{\pi}{2} - \vartheta_0\right) \quad (35)$$

by equation (19), γ becomes

$$\gamma = \Delta\vartheta + \Delta\varphi \quad (36)$$

Furthermore, if ϑ is not too large,

$$\Delta \sin \vartheta \approx \cos \vartheta_0 \Delta \vartheta \quad (37)$$

Temporarily, put

$$\left. \begin{aligned} 4\alpha k_0^2 &= A \\ \sin^2 \vartheta_0 &= a \\ \frac{\beta \cos^2 \vartheta_0}{4\alpha \sin^2 \vartheta_0 + \beta} &= C \\ \Delta\varphi &= x \\ \Delta\vartheta &= y \end{aligned} \right\} \quad (38)$$

so that equation (13) can be written

$$J \propto K e^{-A[a(x+y)^2 + cy^2]} \quad (39)$$

By equation (28):

$$f(x) = K \int_{-\infty}^{+\infty} e^{-A[a(x+y)^2 + cy^2]} y \, dy = -\frac{Kax}{c+a} \sqrt{\frac{\pi}{A(c+a)}} e^{-\frac{Aacx^2}{c+a}} \quad (40)$$

Since f is an odd function of $\Delta\varphi$, the first integral in equation (33) vanishes:

$$\overline{C\xi^2} = \frac{Ns}{2} \frac{K^2 a^2 \pi}{A(c+a)^3} \int_{-\infty}^{\infty} \sin \varphi \cdot (\Delta\varphi)^2 e^{-\frac{2Aac(\Delta\varphi)^2}{c+a}} d(\Delta\varphi) \quad (41)$$

Because only crystals with angles $\varphi \approx \varphi_0$, that is, small $\Delta\varphi$, will contribute to the intensity, $\sin \varphi \approx \cos \vartheta_0$ may be considered as a constant in the integral of equation (41):

$$\begin{aligned} \overline{C\xi^2} &= \frac{Ns\pi K^2 a^2}{2A(c+a)^3} \cos \vartheta_0 \frac{\sqrt{\pi}}{4} \left(\frac{c+a}{2acA} \right)^{3/2} \\ &= \frac{K^2 Ns \cos \vartheta_0}{8A^{5/2}} \left[\frac{\pi}{2ac(c+a)} \right]^{3/2} \end{aligned} \quad (42)$$

The quantity C is now evaluated. By equations (29) and (21)

$$C = \left(\sum n_i \int J(\varphi_i, \vartheta) \, d\vartheta \right)^2 = \left(\sum n_i g(\varphi_i) \right)^2 \quad (43)$$

where

$$g(\varphi) = \int J(\varphi, \vartheta) \, d\vartheta = K \int_{-\infty}^{+\infty} e^{-A[a(x+y)^2 + cy^2]} y \, dy \quad (44)$$

by equation (39). Thus,

$$g(\varphi) = K \sqrt{\frac{\pi}{A(a+c)}} e^{-\frac{Aac(\Delta\varphi)^2}{c+a}} \quad (45)$$

As before, the sum (43) is split into two parts:

$$\begin{aligned} C &= \overline{\sum_{i \neq k} n_i n_k g(\varphi_i) g(\varphi_k)} = \sum_{i \neq k} \bar{n}_i \bar{n}_k g(\varphi_i) g(\varphi_k) + \sum_i \bar{n}_i^2 f^2(\varphi_i) \\ &= \sum_{i \neq k} \left(\frac{Ns}{2}\right)^2 \sin \varphi_i \sin \varphi_k g(\varphi_i) g(\varphi_k) \Delta^2 + \\ &\quad \sum_i f^2(\varphi_i) \left[\frac{s \Delta N \sin \varphi_i}{2} + \left(\frac{s \Delta N \sin \varphi_i}{2} \right)^2 \right] \end{aligned} \quad (46)$$

and taken to the limit $\Delta \rightarrow 0$ so that the second term of the second sum in equation (46) vanishes:

$$C = \left(\frac{Ns}{2}\right)^2 \left(\int \sin \varphi g(\varphi) d\varphi \right)^2 + \frac{Ns}{2} \int g^2(\varphi) \sin \varphi d\varphi \quad (47)$$

If $Ns \gg 1$, which is always implicitly assumed, the second term in equation (47) becomes negligibly small. Replacing again $\sin \varphi$ by $\cos \vartheta_0$,

$$\begin{aligned} C &= \left(\frac{Ns}{2}\right)^2 \cos^2 \vartheta_0 \frac{K^2 \pi}{A(a+c)} \left(\int_{-\infty}^{+\infty} e^{-\frac{Aacx^2}{c+a}} dx \right)^2 \\ &= \frac{1}{ac} \left(\frac{Ns \cos \vartheta_0 K \pi}{2A} \right)^2 \end{aligned} \quad (48)$$

With this value and from equation (42):

$$\overline{\xi^2} = \frac{1}{N s \cos \vartheta \sqrt{\pi A a} 2^{5/2} (a + c)^{3/2} c^{1/2}} \quad (49)$$

or, substituting the definitions (38),

$$\overline{\xi^2} = \frac{(4\alpha \sin^2 \vartheta + \beta)^2}{2^{7/2} N s \cos^2 \vartheta \sin \vartheta \sqrt{\alpha \beta \pi} (4\alpha \sin^4 \vartheta + \beta)^{3/2} k_0} \quad (50)$$

DISCUSSION OF RESULTS

An immediate consequence of equation (50) is that the mean deviation $(\overline{\xi^2})^{1/2}$ is inversely proportional to the square root of the number N of diffracting crystal grains. This result was to be expected on general grounds.

For a given number N, the mean deviation increases like $\frac{1}{\sqrt{\alpha}}$ or $\frac{1}{\rho}$ (equation 5) if α is small. For small crystal dimensions ρ the deviation is inversely proportional to ρ . For large crystals, the mean deviation tends toward:

$$(\overline{\xi^2})^{1/2} = \frac{1}{\sqrt{k_0} 2^{7/4} (N s \sin \vartheta \cdot \beta \pi)^{1/2} \cos \vartheta} \quad (51)$$

Follow the change of $(\overline{\xi^2})^{1/2}$ as a function of α . If ϑ is large, $\sin \vartheta \approx 1$ may be assumed and equation (50) becomes:

$$\overline{\xi^2} = \frac{1}{N s k_0 2^{7/2} \sqrt{\beta \pi} \cos^2 \vartheta \sin \vartheta} \sqrt{\frac{4\alpha + \beta}{\alpha}} \quad (52)$$

The deviation decreases monotonically with increasing α . It will have twice its minimum value

$$2 \left(\frac{2}{N s k_0 \sqrt{\beta \pi} \cos^2 \vartheta \sin \vartheta} \right)^{1/2}$$

when

$$\alpha = \frac{\beta}{56}$$

or

$$\rho = \sqrt{\frac{\beta}{8.16 \times 56}} \quad (53)$$

For copper $K\alpha_1$ radiation, $\beta = 0.458 \times 10^{-8}$, so that

$$\rho = 3 \times 10^{-6} \text{ centimeter}$$

For values much smaller, the deviation increases rapidly; but for larger values of ρ , the deviation decreases only slowly. While it is desirable to make the crystal size large for a given number N , an increase of the grain dimension beyond 10^{-5} centimeter = $1/10 \mu$ does not increase the accuracy noticeably.

So far, the number of crystal grains has been considered as independent of the grain size. In most cases, however, the irradiated volume rather than the number N is constant. When the sample is sufficiently thick, this volume V is the product of irradiated area σ and the effective depth of penetration t given by the absorption of X-rays. Then,²

$$\frac{4\pi}{3} \rho^3 N = V \quad (54)$$

²This assumes that the grains occupy a continuous volume which is not literally possible for spherical grains. However, the assumption of spherical form is arbitrary and in bulk material the grains are actually shaped so as to fill a continuous volume.

or

$$N = V \left(\frac{\pi}{\alpha} \right)^{3/2} \quad (55)$$

If $\sin \vartheta \approx 1$ is again put in the factors including α in equation (50),

$$\overline{\xi^2} = \frac{\alpha \sqrt{4\alpha + \beta}}{2^{7/2} \cos^2 \vartheta \sin \vartheta \sqrt{\beta} \cdot sV\pi^2 k_0} \quad (56)$$

For a given irradiated volume, the mean deviation increases monotonically with the grain size. In particular, for small grain sizes ($4\alpha \ll \beta$), the mean deviation $(\overline{\xi^2})^{1/2}$ is proportional to the grain radius.³

The quantity of main interest is the error in lattice-parameter measurement $\Delta d/d$. From Bragg's law

$$\lambda_0 = 2d \sin \vartheta_0$$

the following relation is obtained by logarithmic differentiation

$$\left| \frac{\Delta d}{d} \right| = \cot \vartheta_0 \left| \Delta \vartheta \right| \quad (57)$$

If ϑ_0 is measured in the fashion described, that is, as the centroid of the intensity curve, the error $\Delta \vartheta$ equals the quantity ξ . The mean deviation becomes:

$$\left| \frac{\Delta d}{d} \right| = \cot \vartheta \sqrt{\overline{\xi^2}} = \left(\frac{\lambda_0 \alpha}{sV \sqrt{\beta}} \right)^{1/2} \frac{4\alpha \sin^2 \vartheta + \beta}{2^{7/4} \pi (\sin \vartheta)^{3/2} (4\alpha \sin^4 \vartheta + \beta)^{3/4}} \quad (58)$$

³This result should not be taken literally for extremely small grain sizes ($\rho \approx 10^{-7}$ cm) because our calculation supposes nonoverlapping lines and fails when the lines become too broad.

by equations (50) and (55). An example of this relation is given in table I. Clearly, the relative error $\Delta d/d$ again increases with increasing grain size and for small grains the error is proportional to the grain radius.

How the relative error depends on the Bragg angle will now be considered. For very small angles ϑ , the relative error becomes very large because of the factor $(\sin \vartheta)^{-3/2}$. However, for medium large angles ($\approx 80^\circ$) there is only a slight variation of the error, and there is no noticeable advantage in using extremely large angles such as $87\frac{1}{2}^\circ$. High angles merely serve to bring out more clearly the details of the erratic intensity fluctuation.

If the grain radius is of the order of 10^{-6} centimeter or larger and ϑ is of the order of 45° or larger, then $4\alpha \sin^2 \vartheta \gg \beta$ and

$$\left| \frac{\Delta d}{d} \right| = \left(\frac{\lambda_0}{sV\sqrt{\beta}} \right)^{1/2} \frac{\alpha^{3/4}}{2^{3/4} \pi (\sin \vartheta)^{5/2}} \quad (59)$$

As an example, take the irradiated area to be 1 square millimeter, the effective depth of penetration as 10^{-3} centimeter, $\beta = 5 \times 10^{-9}$, and $\sin \vartheta \approx 1$. Equation (59) reduces to

$$\left| \frac{\Delta d}{d} \right| \approx \frac{1}{2} \rho^{3/2}$$

or, for crystal radii $\rho \approx 10^{-4}$, $\left| \frac{\Delta d}{d} \right| \approx 10^{-6}$. This is an accuracy about 10 times better than that reported in experimental literature (reference 3). It may be concluded that, by eliminating all sources of error not due to the grain statistics, the accuracy could be improved by a factor of 10, for grains of the order of 10^{-4} centimeter and 1-square-millimeter irradiated area.

Only speculations can be made as to the main cause of error in actual measurement. It would seem that the most important factor not inherent in the crystal grain statistics is the graininess of the recording film.

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TABLE I

VARIATION IN MEAN ERROR OF LATTICE-PARAMETER

MEASUREMENT WITH GRAIN SIZE

[Iron-cobalt $K\alpha$ radiation; θ , 80.64° ; w , 0.81×10^{-11} cm;
irradiated area, 1 sq mm; effective depth, 0.02 mm]

Crystal radius, ρ (cm)	Mean error of lattice- parameter measurement, $\left \frac{\Delta d}{d} \right $
5×10^{-2}	75×10^{-4}
10^{-2}	6.5×10^{-4}
5×10^{-3}	2.3×10^{-4}
10^{-3}	2.1×10^{-5}
10^{-4}	6.7×10^{-7}



